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ISOMER COMPOSITION OF PHOTOSYNTHETIC HYDROBENZOIN*

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Swan and Wright (1) established by the incontrovertible method of isotope dilution analysis that the radiolysis of benzyl alcohol, alone or mixed with acetone, produced meso- and dl-hydrobenzoin in nearly equal amounts. They noted by way of contrast that the action of sunlight on benzyl alcohol in acetone had been reported by Ciamician and Silber (2) to form mainly the meso product. This older qualitative observation, inconsistent with the thesis that in either case the product is formed by radical dimerization, might be discounted were it not that a high degree of photochemical stereospecificity is re-affirmed in more recent work. Leuschner and Pfordte (3) claimed that none of the dl form was produced in the photolysis of pure benzyl alcohol. In another reaction, in which the dimerizing radical is generated by the thermal decomposition of di-t-butyl peroxide in benzyl alcohol, Schwetlick and co-workers (4) reported that the product was "vorwiegend Racemat."

With the object of resolving these inconsistencies the products from the photochemical and the peroxide-induced

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oxidative coupling of benzyl alcohol have been submitted to a gas chromatographic determination of isomer content. The procedure involved conversion to the bis-trimethylsilyl ethers and fractionation of these on a Carbowax-20M column (5) (15 ft.) at 160° on which the retention times were 54 mins. for the meso ether and 58 minutes for the dl form. Essentially quantitative formation of the trimethylsilyl derivatives was achieved on treatment of a 50 mg. specimen of hydrobenzoin in 4 ml dry pyridine with 0.8 ml hexamethyldisilazane and 0.4 ml chlorotrimethylsilane followed by refluxing for 3 hours.

Analytical specimens of the two derivatives were prepared from pure meso- and dl-hydrobenzoin and were purified by recrystallization from aqueous alcohol, then from petroleum ether and finally vacuum sublimation. The bis-trimethylsilyl ether of meso-hydrobenzoin melted at 81.5°. Anal. Calc. for $C_{20}H_{30}Si_2O_2$: C, 66.98; H, 8.43; Found: C, 67.13; H, 8.20. The bis-trimethylsilyl ether of dl-hydrobenzoin melted at 46-46.5°. Anal. Calc. for $C_{20}H_{30}Si_2O_2$: C, 66.98; H, 8.43; Found: C, 67.37; H, 8.46.

The specimens analyzed for meso: dl ratio were the crude non-volatile residues from (1) exposure, under nitrogen, of 2% benzyl alcohol in acetone to sunlight during two days, two different preparations giving identical results within 0.1%: meso, 51.4%; dl, 48.6%, (2) exposure, under nitrogen, of pure benzyl alcohol, in quartz, to a mercury resonance lamp: meso, 50.2%; dl, 49.8%, (3) heating 5 ml di-t-butyl peroxide in 70 ml benzyl alcohol at 135° for 20 hours: meso 51.7%; dl, 48.3%.

It would appear from the measurements that the earlier claims as to stereospecificity must have been based on subjective observations as to crystallinity. There is clearly no marked steric differentiation in the dimerization and there is no significant difference, in the isomeric composition as between products from photolysis and radiolysis.

REFERENCES

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5. The Carbowax-20M column packing (2.5% on Chromosorb G) was the only one of several tried that was effective for this separation. The superiority of Carbowax-20M for the resolution of trimethylsilyl ethers has also been noted by L. Birhofer and A. Ritter, Angew. Chem., 77, 414 (1965).